

REPORT DQ. JMENTATION PAG

AFRL-SR-BL-TR-98-

'88

Public reporting burden for this collection of information is estimated to average 1 hour per response, including gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Service, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Project, Washington, DC 20503-2970.

0236

data sources
or aspect of this
collection of information

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE		3. REPORT TYPE AND DATES COVERED FINAL 15 Sep 96 to 14 Sep 97	
4. TITLE AND SUBTITLE SOLIDS-NMR APPARATUS FOR MATERIALS CHARACTERIZATION				5. FUNDING NUMBERS F49620-96-1-0204 3484/US 61103D	
6. AUTHOR(S) T.C. SANDRECZKI					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) DEPT OF CHEMISTRY UNIVERSITY OF MISSOURI--KC 5100 ROCKHILL ROAD KANSAS CITY MO 64110				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NL 110 DUNCAN AVE ROOM B115 BOLLING AFB DC 20332-8050 DR CHARLES Y-C. LEE				10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES					
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Acquire solids-nuclea magnetic resonance (solids-NMR) capability to enable characterization of polymers and other solid-state materials of relevance to DoD. Instrumentation Acquired: A solids-NMR accessory was acquired for an existing Bruker AC250 1H resonance at 250 MHz) liquids-NMR spectrometer. The acquired equipment included: (a) 35 W buffer amplifier, (b) 120 W radio frequency (RF) amplifier for 1H decoupling, (c) 300 W broadband rf amplifier for non- 1H nuclei, and (d) 7 mm-sample-diameter (0.300 ml sample volume) cross polarization/magic-angle spinning (CP/MAS) probe with pneumatic control unit. The apparatus was installed and tested by specialists from Bruker Instruments, Billerica, MA. Research Supported by Instrumentation: The first solid sample investigated using the newly acquired apparatus was the monomer 1,5,7,11-tetraoxospiro[5,5]undecane, commonly called spiroorthocarbonate(0,0). This is an example of a monomer that polymerize without reduction in volume. Research to be Supported by Instrumentation: Solids-NMR will be used to help determine the structures of organic polymers and inorganic solid-state materials of relevance to DoD. The polymers include ladder- and semi-ladder-shaped highly conjugated polymers and their monomers, and polyurethan coating materials. The inorganic solids include catalytic solids and ferrierites. Relevant nuclei are: 27Al(65 MHz), 13C(65 MHz), 29Si(50 MHz) and 15N(25 MHz).					
14. SUBJECT TERMS				15. NUMBER OF PAGES	
DTIC QUALITY INSPECTED				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT (U)		18. SECURITY CLASSIFICATION OF THIS PAGE (U)		19. SECURITY CLASSIFICATION OF ABSTRACT (U)	
				20. LIMITATION OF ABSTRACT (UL)	

19980317 090

Final Technical Report

December 14, 1997

Grant No. F49620-96-1-0402

Solids-NMR Apparatus for Materials Characterization

PI: T.C. Sandreczki
Department of Chemistry
University of Missouri--KC
5100 Rockhill Rd.
Kansas City, MO 64110

Solids-NMR Apparatus for Materials Characterization

Abstract

Objective: Acquire solids-nuclear magnetic resonance (solids-NMR) capability to enable characterization of polymers and other solid-state materials of relevance to DoD.

Instrumentation Acquired: A solids-NMR accessory was acquired for an existing Bruker AC250 (^1H resonance at 250 MHz) liquids-NMR spectrometer. The acquired equipment included: (a) 35 W buffer amplifier, (b) 120 W radio frequency (rf) amplifier for ^1H decoupling, (c) 300 W broadband rf amplifier for non- ^1H nuclei, and (d) 7 mm-sample-diameter (0.300 ml sample volume) cross polarization/magic-angle spinning (CP/MAS) probe with pneumatic control unit. The apparatus was installed and tested by specialists from Bruker Instruments, Billerica, MA.

Research Supported by Instrumentation: The first solid sample investigated using the newly acquired apparatus was the monomer 1,5,7,11-tetraoxospiro[5,5]undecane, commonly called spiro*ortho*-carbonate(0,0). This is an example of a monomer that polymerizes without reduction in volume.

Research to be Supported by Instrumentation: Solids-NMR will be used to help determine the structures of organic polymers and inorganic solid-state materials of relevance to DoD. The polymers include ladder- and semi-ladder-shaped highly conjugated polymers and their monomers, and polyurethane coating materials. The inorganic solids include catalytic zeolites and ferrierites. Relevant nuclei are: ^{27}Al (65 MHz), ^{13}C (63 MHz), ^{29}Si (50 MHz), and ^{15}N (25 MHz).

Solids-NMR Apparatus for Materials Characterization

Objective

Acquire solids-nuclear magnetic resonance (solids-NMR) capability to enable characterization of polymers and other solid-state materials of relevance to DoD.

Performance on Contract

Summary: With the funds provided by this contract (\$50,440) plus matching funds from the University of Missouri--KC (UMKC) (\$24,000) the Department of Chemistry has acquired a solids-NMR accessory for the existing 250 MHz liquids NMR spectrometer (Bruker AC250). This solids accessory makes use of the cross polarization/magic-angle spinning (CP/MAS) technique to enable acquisition of liquids-like spectra from solid materials.

Previously-existing equipment: Prior to acquisition of the solids accessory, the Department of Chemistry at UMKC owned a Bruker AC250 (^1H resonance at 250 MHz) NMR spectrometer. This is the only Fourier transform spectrometer located at the Kansas City campus. The AC250 has served the Department of Chemistry well as a liquids instrument, but it has been incapable of solids experiments. The AC250 is one of the best-supported instruments in the Department of Chemistry. Approximately \$15,000 was spent in 1994-95 to provide the AC250 spectrometer a room of its own, with its own air conditioning and humidity control.

Description of equipment acquired under this contract:

Number	Item	Description	Model	Cost
1	Level I Solids Accessory for Bruker AC250	(See detail in 1a-1g.)		\$30,900
1a	BLARH 100	Linear array amplifier for ^1H observe and homo/heteronuclear ^1H decoupling; 100W linear pulse power, 10W linear CW, 0.8 W ultra linear state, all operations under computer control with total dynamic excitation range >120dB.	BLAH100	
1b	BLAX 300 RS	Linear broadband amplifier for X nucleus pulse and decouple with ultra-fast blanking and rise/fall times; 300 W linear pulse power, 30 W linear CW, all operations under computer control.	BLAX300	

Number	Item	Description	Model	Cost
1c	MAS Matching Assembly 300	Impedance matching assembly	Z00556	
1d	Directional Coupler	Directional coupler--crossed diode assembly	X	
1e	Magic Angle Spinning (MAS) Control Unit	Microprocessor based MAS control unit with spinning rate counter, precision regulating valves, pressure stabilization and sample eject.	H2620	
1f	Instrument Rack	To hold amplifiers and MAS control unit*	X	
1g	XWIN-NMR	Solids analysis software upgrade	H5548	
2	VT CPMAS Probe	Multinuclear probe tuning from ^{15}N to ^{31}P , doubly tuned for ^1H cross-polarization, 7mm rotor design with 8 kHz maximum spinning speed, VT range -50 to +120 (?) $^{\circ}\text{C}$.	K3157	\$25,050
3	MAS Heat Exchanger	Heat exchanger required for MAS experiments above and below ambient temperature.	W1100881	\$2,400
4	Decoupler Upgrade	Decoupler upgrade to 35 W, including fast switching capability.	W1300075	\$7,200
5	MAS Probe Starter Kit	Includes 3 rotors, six Kel-F caps, three ZrO caps, packing rod and cap-removal tool.	B1762	\$1,750
6	Extra Rotors	3 extra rotors with Kel-F caps.	B200156	\$750
7	Extra Kel-F Caps	3 extra Kel-F caps.	B200159	\$150
8	Extra ZrO Caps	3 extra zirconia caps.	B200158	\$600
9	Shipping			\$299
10	Installation	Includes travel plus labor		\$5341
TOTAL				\$74,440

* Note: The Instrument Rack was not required and is being returned to Bruker. In its place, Bruker has granted us \$2000 worth of consumables. These will include (as needed) rotors, switching diodes, and a back-up directional coupler.

The acquired solids accessory has several components: (1) The Decoupler Upgrade is a 35 W amplifier that enables the AC250 spectrometer to drive the new high-power amplifiers. (2) The BLARH 100 is a 120 W amplifier that provides effective spin-locking of the ^1H nucleus during cross-polarization, and provides high powered, CW proton decoupling during data acquisition from the X nucleus (e.g., ^{13}C). (This decoupling results in rapid averaging of dipolar interactions between ^1H and the X nuclei, and thus minimizes this source of line broadening.) (3) The BLAX 300 RS is a 300 W amplifier that provides high power rf to the X nuclei during the cross-polarization period. (During cross polarization, spin polarization from ^1H nuclei is transferred to the observed X nuclei.) (4) The VT CPMAS Probe accommodates a relatively large 7 mm-diameter (0.300 ml volume) sample. The trade-off for this large sample volume is a low spinning speed (only 8 kHz). However, this trade-off is ideal for the existing, relatively low frequency 250 MHz spectrometer: The large sample volume improves sensitivity, and the 8 kHz spinning is well suited to averaging the smaller anisotropic chemical shifts associated with the 250 MHz spectrometer. The probe is dual tuned to ^1H (fixed) plus the X nucleus (variable from ^{15}N through ^{31}P). Together the proton decoupling and magic angle spinning enable high resolution NMR spectra to be obtained from solid samples. (5) The MAS Matching Assembly, and the Directional Coupler are for impedance matching and routing of signals, respectively. (6) The Magic Angle Spinning Control Unit uses optical feedback and precision valves to maintain the sample spinning rate to within 2 Hz of the set rate. (7) The MAS Heat Exchanger enables variable temperature operation from -50 to 120(?) $^{\circ}\text{C}$.

Special Circumstances:

There were minor special circumstances involved in the acquisition and installation of the solids-NMR accessory. 1) Because the solids-NMR upgrade was a hybrid custom/off-the-shelf accessory for the Bruker AC250 spectrometer, it took seven months ARO for the accessory to be delivered. 2) Because our existing instrument rack was sufficient to accommodate the new amplifiers, we were able to return the new instrument rack to Bruker in exchange for \$2000 in consumables (to be ordered as needed). These include: switching diodes, back-up directional coupler, rotors.

Use of the acquired equipment to date:

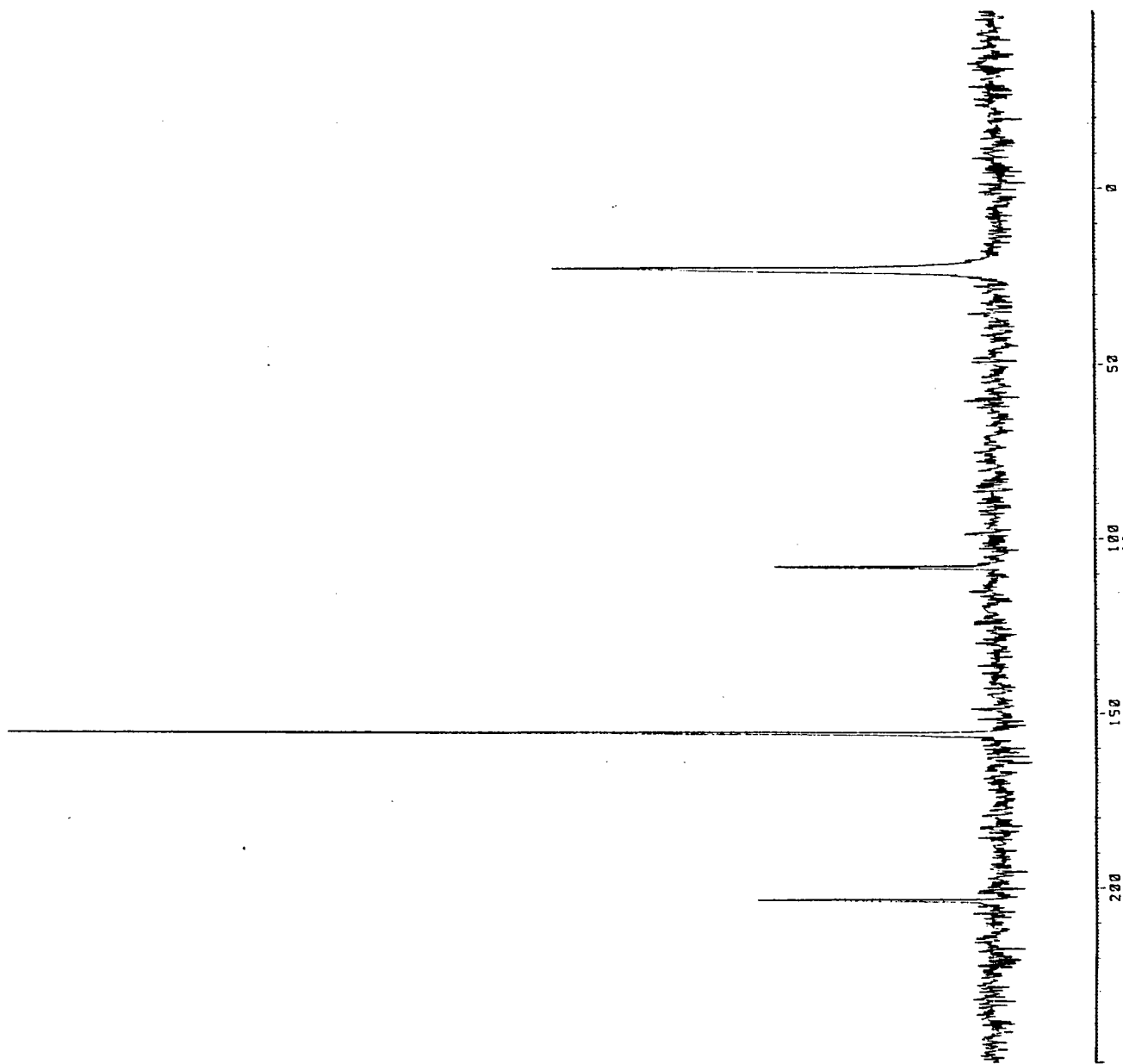
The solids-NMR accessory has been installed and verified for performance by a Bruker specialist. Magic angle spinning was optimized using samples of KBr and adamantane. Amplifier powers were matched for optimization of cross polarization using adamantane. Initial magnet shimming was optimized using adamantane, and the shim file was recorded. Instrument performance was evaluated using a standard glycine sample. (See Fig. 1.)

The first research sample examined by solids-NMR was submitted by Prof. A.J. Holder, Department of Chemistry, UMKC. The sample was the monomer 1,5,7,11-tetraoxospiro[5,5]-undecane, commonly called spiroorthocarbonate(0,0). (See Fig. 2.) This sample has three chemically distinct carbons in a 1:2:4 ratio. The spectrum, which required ~15 min to acquire, has three lines corresponding to the three carbons. Impurity content is negligible. (See Fig. 2.)

Samples to be examined in the immediate future:

The next samples to be examined by solids-NMR include the following: 1) polymerized samples of the spiroorthocarbonate(0,0) monomer, 2) *cis* and *trans* monomers of ladder-shaped highly conjugated polymers, 3) ladder- and semi-ladder-shaped highly conjugated polymers, 4) polyurethane coatings being evaluated under AFOSR contract F49620-97-1-0162 (Characterization of Aging-Induced Physical and Chemical Defects in Aircraft Long-Life Coating Systems). In general, the solids-NMR apparatus significantly enhances our materials characterization capabilities.

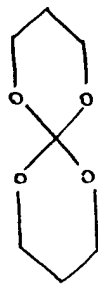
Fig. 1 GLYCINE, ^{13}C MEASURED BY CPMAS SEQUENCE, NOV 12 1997



~~EXPER~~
 GLYCINE
 AU: 100.00
 CPMAS: AU
 DATE 12-11-97
 SF 62.998
 ST 62.9
 Q1 3505.000
 SI 4096
 TO 1500
 SW 75000.000
 HZ/PT 12.207
 PW 0.3
 RC 0.3
 RG 10.032
 NS 4
 TE 293
 FM 31300
 DZ 4931.000
 CP 22L 00
 LB 0.3
 GB 0.0
 CX 25.00
 CY 0.3
 F1 250.1280
 F2 -49.9170
 HZ/CM 751.983
 PPM/CM 12.002
 SR 2425.19

Fig. 2 SOC00, MEASURED BY CPMAS, 12 NOV 97

~~SECRET~~
 SOC00.001
 AU PROG: CPMAS-AU
 DATE 12-11-97
 SF 62.896
 ST 62.896
 Q1 3585.000
 S1 4096
 T0 1500
 SW 25000.000
 HZ/PF 12.207
 PW 0.0
 RO 0.0
 RG 10.030
 RS 64
 TE 295
 FM 31300
 QZ 4931.000
 CP 22L DC
 LB 0.0
 GB 0.0
 GCX 25.00
 CT 0.0
 FI 200.005P
 FZ -49.972P
 HZ/CM 628.906
 PPM/CM 9.998
 SR -1701.55



SOC00

